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(54) Oxidation Resistant Magnesium
Alloys

(57) Magnesium alloys containing up
to 12% aluminum, up to 1.5% zinc, up

to 1.5% silicon, up to 0.18%
manganese, 0.0025% to 0.015%
beryllium are die cast without need for
protective flux coverings. Die cast
products that do not contain harmful
flux inclusions are produced thereby.

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SPECIFICATION Oxidation Resistant Magnesium Alloy

The invention generally relates to magnesium alloys that contain beryllium and are sufficiently resistant to oxidation in the molten condition to obviate the need for the use of protective flux covers to prevent excessive melt oxidation or burning when exposed to oxygen-containing atmospheres. Beryllium functions to reduce the propensity of molten magnesium alloys to oxidize when exposed to oxygen-containing atmospheres such as air.

The elimination of the need to employ a protective flux cover for molten magnesium alloys is advantageous from at least several respects. First of all, the elimination of flux covers results in a significant cost reduction. In addition, the absence of flux covers means that flux particles cannot become mixed into the molten magnesium metal and then become trapped in the resultant casting in the form of flux inclusions. The lack of flux covers also results in increased magnesium yields because of the lack of entrapment and subsequent loss of molten magnesium in the flux covering.

It is known in the art to add beryllium to magnesium base alloys for various purposes. United States Patent Numbers 2,380,200; 2,380,201; 2,383,281; 2,461,229 and 3,947,268 as well as an article by F. L. Burkett entitled "Beryllium in Magnesium Die Casting Alloys" which appeared in *AFS Transactions*, Volume 62, pages 2—4 (1954) disclose the addition of beryllium to magnesium base alloys. Of the above cited information, United States Patent Numbers 2,380,200 and 2,380,201, and the Burkett article teach that beryllium reduces the propensity for molten magnesium alloys to oxidize. These prior efforts to reduce oxidation do not involve beryllium additives at the levels of the invention and do not appear to involve the imposition of a restriction of manganese content to permit increased beryllium solubility in the magnesium alloy. Moreover, the Burkett article suggests that higher beryllium levels must be avoided.

The magnesium alloys of the invention comprise up to about 12% aluminum, up to about 1.5% zinc, up to about 1.5% silicon, up to about 0.18% manganese, from about 0.0025% to 0.015% beryllium, balance essentially magnesium. All compositional percentages are stated in weight percent. It is preferred to restrict the manganese content to a maximum of about 0.05% when the beryllium content ranges between about 0.012% and 0.015% to increase the solubility of beryllium in molten magnesium to an extent sufficient to enable the above mentioned amount of beryllium to be dissolved in the magnesium. For example, about 0.15% manganese will permit the dissolution of from about 0.007% beryllium in molten magnesium.

It is preferred to maintain manganese from about 0.04% to 0.15% and beryllium from about 0.005% to 0.0125% in the magnesium alloys of the invention to enhance corrosion resistance of the alloy. It is further preferred to restrict manganese from about 0.08% to 0.15% and beryllium from about 0.006% to 0.01% to further enhance corrosion resistance of the magnesium alloys.

The principles of the invention are readily adaptable for use in the production of magnesium alloy die casting. Magnesium die casting alloys typically contain from 1% to 12% aluminum, up to 1.5% zinc, up to 1.5% silicon, from 0.2% to 1.0% manganese, balance essentially magnesium.

The manganese content of the alloys of the invention is important because of its influence upon the solubility and ease of alloying of beryllium in molten magnesium. Because this influence was not heretofore recognized, AZ91B, a widely used die casting alloy having a nominal composition of 9% aluminum, 0.7% zinc, 0.2% manganese, 0.5% silicon maximum, 0.3% copper maximum, 0.03% nickel maximum, balance essentially magnesium has contained less than 0.001% beryllium. It has been discovered that beryllium is soluble in AZ91B magnesium alloys to an extent greater than previously believed. In any event, a beryllium level of on the order of 0.001% is considered to be inadequate for purposes of achieving good protection of the molten magnesium. Rather it has been determined that about 0.0025% to about 0.015% beryllium should be dissolved in molten magnesium or its alloys to inhibit burning, with the amount of beryllium being increased with increasing oxygen content of the atmosphere. Accordingly, the manganese content should not exceed more than about 0.18%, preferably no more than about 0.15%. When nitrogen atmospheres and short exposure times are involved, additions of from about 0.0025% to 0.005% beryllium are sufficient to provide protection of molten magnesium. However, when longer exposure times or significant air leakage into the nitrogen atmosphere occurs, beryllium contents on the order of from about 0.005% to 0.01% are recommended. On the other hand, should it be desired to inhibit the burning of molten magnesium or magnesium alloys held in air, a beryllium content of about 0.012% to 0.015% is preferred. Such beryllium contents require manganese to be restricted to no more than about 0.05%.

The beryllium level used depends upon the amount of oxygen in the atmosphere over the melt. For example, if the molten magnesium is exposed to air without a cover, the oxygen content of the atmosphere will remain at about 20%, and, accordingly, high beryllium levels, on the order of 0.01% to 0.015%, will be needed to avoid excessive oxidation or burning. Should the molten magnesium be exposed for prolonged periods, it may be desirable to periodically add beryllium to compensate for beryllium that is oxidized or to add larger amounts of beryllium; e.g., 0.02% in order that the excess above the solubility limit will gradually dissolve to compensate for oxidation losses and thereby maintain the beryllium at or close to the saturation level in the molten magnesium.

To reduce the beryllium level required for good melt protection it is desirable to keep the oxygen level as low as is practical. Placement of a lid or hood over the molten magnesium is helpful in this regard. Reaction of the molten metal with oxygen in the enclosed air will lower the oxygen content of the atmosphere. If the system is very tight and the resultant oxygen content becomes very low, beryllium levels as low as 0.0025% will provide adequate protection. If the system is not tight or is periodically opened for brief periods for operations such as ladling, it may be desirable to introduce sufficient nitrogen or other inert gases to maintain the low oxygen contents. In such situations an intermediate beryllium level, e.g., 0.005% to 0.01%, may be used. Other protective gases such as SF_6 , SO_2 , and various inert gases may also be used, although nitrogen is preferred due to its relative availability.

Impurities such as iron tend to form insoluble intermetallic compounds with beryllium and accordingly should be minimized. Because manganese, when in the presence of aluminum contents on the order of 1% to 12%, forms a relatively insoluble phase with iron which then settles to the bottom of the melt, small quantities of manganese such as 0.1% may be included in die casting alloys for purification purposes. However, the manganese level should not be high enough to precipitate beryllium. Typically, manganese contents should be decreased from 0.18% to 0.05% as the beryllium level increases from 0.0025% to 0.015% in magnesium alloys containing about 9% aluminum.

The following experimental results illustrate certain of the principles of the invention.

A magnesium test alloy containing about 9% aluminum, about 0.7% zinc, and about 0.0025% beryllium was held under a hood for 8 hours without burning or excessive oxidation.

A 130 lb. batch of an alloy containing 7.1% aluminum, 0.71% zinc, 0.05% manganese, balance magnesium was melted, covered with a flux and held under a hood at 1250°F. Following removal of the flux by skimming, burning of the molten alloy occurred after 1 minute. The burning was then extinguished with the establishment of a flux cover. The hood was closed and nitrogen was flooded over the surface of the flux-covered molten bath at a rate of 30 cfh for about 5 minutes. The hood was closed, the flux cover removed, and nitrogen flow was continued at a rate of 30 cfh. After 30 minutes, blooms (localized areas of high oxidation) began to form and increase in size. After 51 minutes the blooms began to burn slowly and emit a bright light. The hood door was then briefly opened periodically to permit ladling and casting of test bars. Burning became more vigorous after 5 minutes of casting and very intense after 15 minutes.

Additional tests were conducted by adding various amounts of beryllium to the molten magnesium test alloy described in the preceding paragraph. In general, the tests indicated that beryllium additions decrease the tendency of the molten alloy to burn. When on the order of 0.008% beryllium was incorporated, the alloy was held satisfactorily under a 30 cfh nitrogen flow and then die cast into test bars. This alloy was also held in air without burning for approximately 15 minutes. As the beryllium content was increased during the various tests, it was noted that the oxidation resistance of the molten magnesium alloy increased and that lessened rates of nitrogen flow were required for satisfactory operation. When about 0.011% to 0.013% beryllium was incorporated into the molten alloy, the surface of the alloy became silvery in appearance and was satisfactorily held under exposure to air and then die cast. When the silvery protective surface film was deliberately disrupted, a new film formed instantly, indicating that the protective function of beryllium was still operative. Following exposure to air for about 1 hour, however, oxide blooms began to form and grow slowly.

When 0.0025% beryllium was alloyed into the magnesium test alloy, the melt was satisfactorily held under a nitrogen flow of 30 cfh with door closed and then was cast into test bars. Following 15 minutes, the molten magnesium alloy was heavily bloomed and commencing to burn. When 0.007% to 0.01% beryllium was alloyed, the casting run was successfully completed without the occurrence of blooming with 60 cfh nitrogen. The door of the hood was then held open for 15 minutes without bloom formation. Nitrogen flow was then stopped and the molten alloy was held for an additional 15 minutes without bloom formation. After the alloy was saturated with about 120—130 ppm beryllium at 1200°—1300°F, it was held in air with the door open for over 30 minutes without bloom formation and was then successfully cast without a nitrogen atmosphere. Extended holding, however, finally led to bloom formation.

To determine the compatibility of manganese and beryllium in magnesium alloys, two AZ91B ingots containing about 0.2% manganese were added to the melt. This addition reduced the beryllium content to about 0.008% and increased the manganese content to 0.12%. The molten alloy was successfully die cast with a flow of 60 cfh nitrogen and the hood door opened only as required. A portion of the melt was poured in air into a large ingot mold. No discoloration was noted on the metal surface as it slowly solidified.

Another AZ91B ingot was added to the molten alloy with a resultant lowering of the beryllium content to about 0.007% and an increase in the manganese level to about 0.15%. Test bars were again cast under 60 cfh of nitrogen. Several blooms had formed at the end of the run.

The variations in manganese and beryllium level had no apparent effect upon the castability of the magnesium test alloy. Some improvement in fluidity and surface appearance appears to result from increasing beryllium content because of less oxidation of the molten material.

Five die cast bars of each alloy were tested in tension to determine the effect of beryllium and manganese. The results set forth in Table I indicate that lower manganese and higher beryllium function to increase both ductility and tensile strength of the magnesium test alloy.

Sanded test bars of each alloy were also immersed in salt water (3% NaCl) for 3 days to determine corrosion resistance. The bars were sanded to remove the cast surface. The results in Table II indicate that beryllium additions reduce the salt water corrosion rate of the magnesium test alloy to the same low level obtained by manganese additions. Small amounts of manganese, e.g., 0.12%, reduce the amount of beryllium required for good corrosion resistance. The improvement effected by beryllium can be attributed to a reduction in iron content.

Table I					
	% Be	% Mn	% E	TYS*	TS*
	0	0.05	6	21,500	36,300
	0.0025	0.05	7	22,900	38,900
	0.0086	0.05	6	22,700	36,800
	0.0113	0.04	7	21,000	38,200
	0.0125	0.04	5	22,000	37,800
	0.0081	0.12	6	22,700	39,000
	0.0071	0.15	8	21,900	40,500
	0.0006**	0.2	4	21,700	34,600

* Pounds per Square Inch.

** (AZ91B).

Table II				
	% Be	% Mn	% Fe	Corrosion Rate-IPY*
	—	0.05	>0.15	1.30
	0.0025	0.05	0.15	0.95
	0.0086	0.05	0.008	0.17
	0.0113	0.04	0.005	0.03
	0.0125	0.04	0.005	0.03
	0.0081	0.12	0.006	0.03
	0.0071	0.15	0.007	0.03
	0.0006**	0.2	0.003	0.03

*inches per year.

** (AZ91B).

- 35 Claims**
1. A magnesium alloy consisting essentially of up to 12% aluminium, up to 1.5% zinc, up to 1.5% silicon, up to 0.18% manganese, from 0.0025% to 0.015% beryllium, balance essentially magnesium.
 2. An alloy as claimed in claim 1, containing from 0.0025% to 0.005% beryllium.
 3. An alloy as claimed in claim 1, containing from 0.005% to 0.01% beryllium.
 4. An alloy as claimed in claim 1, containing from 0.04% to 0.15% manganese and from 0.005% to 0.0125% beryllium.
 5. An alloy as claimed in claim 4, containing from 0.08% to 0.15% manganese and from 0.006% to 0.01% beryllium.
 6. An alloy as claimed in claim 5, containing about 9% aluminium, about 0.7% zinc, about 0.12% manganese, and about 0.008% beryllium.
 7. An alloy as claimed in claim 1, containing not more than 0.05% manganese and from 0.012% to 0.015% beryllium.
 8. An alloy as claimed in any one of claims 1 to 7 containing from 1 to 12% aluminium.
 9. An alloy as claimed in claim 8 in the form of a die casting.
 10. An alloy as claimed in any one of claims 1 to 9 and substantially as hereinbefore described.
 11. A die casting characterized by being essentially free of flux inclusions and consisting essentially of from about 1% to 12% aluminium, up to 1.5% zinc, up to 1.5% silicon, up to 0.18% manganese, from 0.0025% to 0.015% beryllium, balance essentially magnesium.
 12. A die casting as claimed in claim 11 and substantially as hereinbefore described.
 13. A method of making a magnesium alloy die casting, comprising:
 - a. providing a molten pool of a magnesium alloy consisting essentially of 1% to 12% aluminium, up to 1.5% zinc, up to 1.5% silicon, up to 0.18% manganese, from 0.0025% to 0.015% beryllium, balance essentially magnesium,
 - b. die casting said molten magnesium alloy.
 14. A method as claimed in claim 13, wherein the molten pool is exposed to an oxygen-containing atmosphere.

15. A method as claimed in claim 14, wherein the magnesium alloy contains from 0.0025% to 0.005% beryllium and the molten pool is exposed to an atmosphere containing a greater amount of nitrogen than that contained in air.

5 16. A method as claimed either in claim 13 or claim 14, wherein the magnesium alloy contains from about 0.005% to 0.01% beryllium.

17. A method as claimed in claim 14, wherein the magnesium alloy contains from 0.01% to 0.015% beryllium and up to 0.05% manganese and the molten pool is exposed to air.

18. A method as claimed in any one of claims 13 to 17 and substantially as hereinbefore described.

10 19. Magnesium alloy die-castings whenever made by the method claimed in any one of claims 13 to 18.

20. A die-casting as claimed in claim 19 which is substantially free from flux inclusions.

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